

LETTERS

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Anomalous behavior during leveling of thin coating layers with surfactant

L. W. Schwartz,^{a)} R. A. Cairncross, and D. E. Weidner

Department of Mechanical Engineering, University of Delaware, Newark, Delaware 19716

Our recently-published linear analysis [Schwartz *et al.*, *Langmuir* **11**, 3690 (1995)] demonstrated that an initially rippled thin layer of Newtonian liquid with uniformly distributed surfactant may level in unexpected ways. While the presence of surfactant will, in general, slow the rate of leveling compared to that of a perfectly clean system, there was shown to exist a realistic parameter range where increasing, rather than reducing, the amount of surfactant present will hasten leveling. Here, for the two-dimensional problem, we investigate the importance of nonlinearity through numerical solution of (i) the unsteady lubrication form of the evolution equations with surfactant, and (ii) finite-element solution of the exact governing equations for slow viscous flow. Confirmation of the linear results is demonstrated and quantitative discrepancy only appears for large-amplitude and short-wavelength ripples. Surface tension gradient driven flow explains the anomalies; for moderate surfactants, the surface quickly 'hardens,' leading to a decay rate of one-quarter of the clean-surface rate, while for weak surfactants, leveling proceeds to a plateau level which decays much slower than the hard-surface result. © 1996 American Institute of Physics. [S1070-6631(96)03507-6]

The leveling of irregularities of the surface of thin liquid films on solid substrates is vital for successful coating operations, be they for protective or decorative purposes. Surface tension is the principal agent responsible for the leveling of short-wavelength undulations.¹ When surface-active material is present, the rate of leveling is retarded, principally due to the development of a nonuniform distribution of surfactant. Since local values of surface tension are reduced by the presence of surfactant, surface flow during leveling leads to the creation of surface tension gradients. They cause shear stresses at the liquid surface that tend to oppose the leveling. Environmental contamination is typically surface-active and the need for good leveling behavior is a principal reason for extreme cleanliness during coating operations.

It would not seem unreasonable to assume, therefore, that increasing the average amount of surfactant present will cause a monotonic decrease in the rate of leveling. Recently we have shown,² via a linearized analysis, that this is not the case, and, depending on the surface undulation wavelength and the degree of leveling required, more rapid leveling can sometimes be obtained by *increasing*, rather than reducing the amount of surfactant present. Because the linear analysis involves many assumptions, one purpose of this note to ascertain its range of validity and extend the results with the finite element method and the lubrication approximation. We state the full time-dependent problem below, for an assumed liquid layer with insoluble surfactant lying on a flat substrate. Assuming the surface slope to be small leads to a uniformly-valid set of coupled evolution equations, i.e., the so-called lubrication approximation. Graphical results are presented comparing the three methods. Physical mechanisms respon-

sible for the anomalous behavior are then inferred, principally through use of the linearized analysis.

We consider a two-dimensional layer of liquid lying on the solid substrate $y=0$ whose free surface is given by $F(x,y,t)=y-h(x,t)=0$. Initially the surface is sinusoidal, $h(x,0)=h_0+a_0\cos kx$, and the surfactant is uniformly distributed. The subsequent motion obeys the Stokes momentum equation and incompressibility

$$\nabla p = \mu \nabla^2 \mathbf{V}, \quad \nabla \cdot \mathbf{V} = 0 \quad (1a)$$

within the liquid region. In addition to the no-slip condition $\mathbf{V}=\mathbf{0}$ on $y=0$ and imposed symmetry on $kx=0$ and π , we have stress and kinematic conditions on $F=0$. With $\mathbf{\Pi}$, \mathbf{s} , and \mathbf{n} signifying the stress tensor and unit tangent and normal vectors, respectively, these are

$$\mathbf{\Pi} \cdot \mathbf{n} \cdot \mathbf{n} = \sigma \kappa, \quad \mathbf{\Pi} \cdot \mathbf{n} \cdot \mathbf{s} = \nabla_s \sigma, \quad \mathbf{n} \cdot (\mathbf{V} - \dot{\mathbf{x}}) = 0, \quad (1b)$$

where $\dot{\mathbf{x}}$ is the surface velocity. Here p , μ , σ , and κ represent pressure, viscosity, surface tension and surface curvature, respectively. The surfactant is conserved,

$$\frac{\partial c}{\partial t} + \nabla_s \cdot (c\mathbf{u}) = D \nabla_s^2 c, \quad (1c)$$

following e.g., Stone³. Here \mathbf{u} is particle velocity on the surface, D is a surface diffusion coefficient and $\nabla_s = (\mathbf{I} - \mathbf{nn}) \cdot \nabla$ is the surface gradient operator.

The surface tension variation, due to changes in surface concentration c , is assumed to follow the linear law

$$\sigma = \sigma_0 + \Gamma(1 - c). \quad (1d)$$

Initially the surface tension is σ_0 , corresponding to $c=1$. In general Γ will be a positive number. As in Ref. 2, the sub-

strate coordinate is made dimensionless using $(1/k)$ as characteristic length, while y and h are referenced to h_0 , the mean coating depth. The reference time is

$$T^* = \frac{3\mu}{\sigma_0 h_0^3 k^4} \quad (2)$$

which is the characteristic leveling time for a thin liquid layer with a slightly-perturbed clean surface, as shown by Orchard.⁴

The mathematical model has been solved using three approximation techniques, the finite element method (FEM), lubrication theory, and a linearized theory. Lubrication theory and the linearized theory simplify the problem to a form that can be solved with simple numerical techniques. The FEM solves the equations in their fundamental form but approximates the solution by piecewise polynomial functions over elements. Application of the FEM to moving- and free-surface problems in fluid mechanics is now a well established procedure and is discussed elsewhere.⁵⁻⁷ The FEM more accurately (depending on mesh refinement) represents the physics of the solution, but requires much more computational effort. This paper shows that for many coatings (e.g., thin coatings with long wave-length disturbances) the lubrication and linearized results are as accurate as the FEM solutions. That all three methods give the same results over a range of parameters serves as a check for the consistency and accuracy of each method.

The lubrication approximation² is obtained by a systematic expansion in the assumed small parameter $h_0 k$. The equation for surface concentration becomes

$$c_t + (u^{(s)}c)_x = \Delta c_{xx} + O(h_0 k)^2, \quad (3)$$

where $u^{(s)}$ is the surface velocity, strictly in the x -direction to this order, and given by

$$u^{(s)} = \frac{3}{2} h^2 h_{xxx} - R h c_x. \quad (4)$$

The evolution equation for the surface profile is

$$h_t = -(h^3 h_{xxx})_x + \frac{R}{2} (h^2 c_x)_x. \quad (5)$$

Here subscripts signify partial differentiation. The two parameters that appear in the model are

$$R = \frac{3\Gamma}{\sigma_0 h_0^2 k^2}, \quad \Delta = k^2 D T^*. \quad (6)$$

The parameter R is taken to be $O(1)$; thus Γ/σ_0 is $O(h_0 k)^2$ and the deviation of the surface tension from σ_0 has been properly neglected in the first term on the right side of equation (5). For the results below, the coupled system (3)–(5) was solved by a finite-difference method, with convergence verified under spatial and temporal refinement.

The linear model employs a further simplification; the thickness on concentration variations are sinusoidal with amplitudes $\alpha(t)$ and $\gamma(t)$, respectively. For $\alpha(0) = a_0/h_0$, $\gamma(0) = 0$. The full solution of the linear problem is

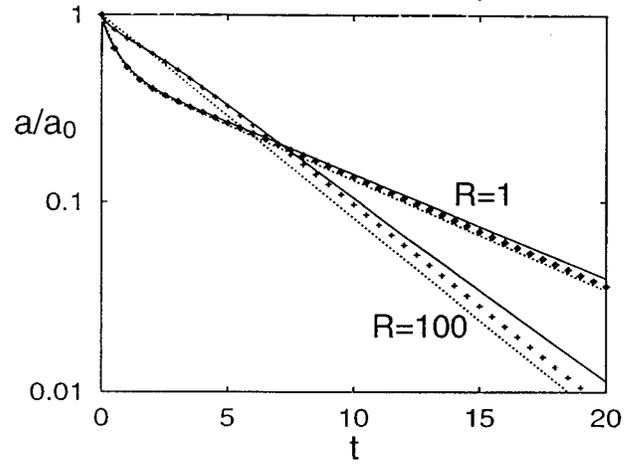


FIG. 1. Ripple crest amplitude versus time for two values of the surfactant strength parameter R with $a_0/h_0=0.5$, and $kh_0=0.126$. A comparison of linear theory (dashed lines), lubrication theory (symbols) and FEM results (solid lines). The larger value, $R=100$, exhibits better leveling at larger times.

$$\alpha/(a_0/h_0) = \exp(\omega_2 t) + [(\omega_2 + 1)/(\omega_2 - \omega_1)] [\exp(\omega_1 t) - \exp(\omega_2 t)], \quad (7a)$$

$$\gamma/(a_0/h_0) = [(3/2)/(\omega_2 - \omega_1)] [\exp(\omega_1 t) - \exp(\omega_2 t)]. \quad (7b)$$

The two eigenvalues $\omega_{1,2}$ are given explicitly as

$$2\omega_{1,2} = -(1 + R + \Delta) \pm [(1 + R + \Delta)^2 - R - 4\Delta]^{1/2}, \quad (7c)$$

where R and Δ are non-negative and the two roots are negative real or zero. Thus all sinusoidal ripples will ultimately decay. Limiting cases, for $\Delta=0$, are $R \ll 1$,

$$\alpha/(a_0/h_0) = (3/4)R + O(R^2 t) + \dots + \exp(-t) + \dots \quad (8)$$

and for $R \gg 1$,

$$\alpha/(a_0/h_0) = \exp(-t/4) [1 - 3/(4R) + O(1/R^2)]. \quad (9)$$

In the large R limit, the decay time is seen to be four times the Orchard value.

In Fig. 1 we show the crest amplitude ratio $a/a_0 = (h(0,t) - 1)/(h(0,0) - 1)$ versus dimensionless time. The three theories are compared for the two cases $R=1$ and $R=100$. For the lubrication and FEM results, the initial amplitude was $a_0/h_0=0.5$. The linear approximation requires that the ripple amplitude be small; thus it is seen to slightly overestimate the rate of leveling for the two cases, while correctly modeling the qualitative behavior. For the FEM solution, the ratio of wavelength to mean depth is 50, corresponding to $kh_0=0.126$. According to any of the three theories, the curves are seen to cross at about $t=7$ where the amplitude has decayed to about 20% of its initial value. At $t=20$, the $R=100$ case, for which the surfactant effect is very much stronger, shows a ripple amplitude that is only about one-third of the $R=1$ value. The apparent divergence of the $R=100$ results for small values of a/a_0 is due essentially to the nature of the plot; calculated values of h differ only by about 10^{-3} , consistently for both R values.

Figure 2 shows profiles of the free surface h , concentration c and surface velocity $u^{(s)}(x)$ at the early time $t=0.5$ for

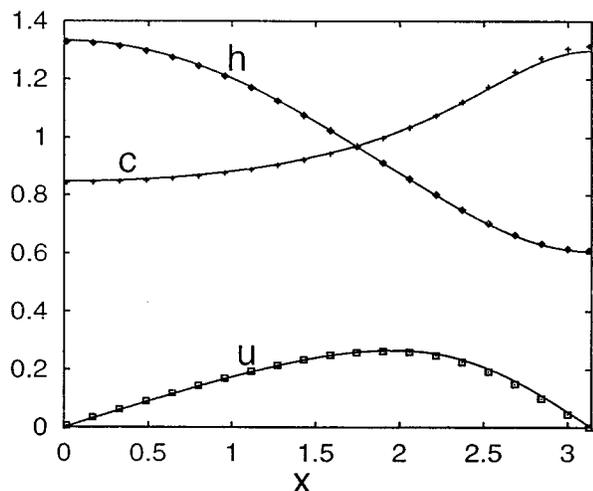


FIG. 2. Calculated surface shape, concentration profile, and surface speed distribution at the time $t=0.5$; Lubrication theory (symbols) and FEM (lines) are compared. Here $R=1$, $a_0/h_0=0.5$, and $kh_0=0.126$.

$R=1$ and $a_0/h_0=0.5$. The surface velocity is towards the trough which causes a rise in surfactant concentration there and a resultant tension-gradient stress directed towards the crest. Each curve shown is markedly nonsinusoidal, differing, in this way, from the linear theory. The lubrication and FEM results are compared and are in substantial agreement. An equivalent plot for $R=100$ (not shown) would reveal that the concentration is essentially constant and $u^{(s)}(x) \approx 0$. That is, for large values of R , the surface “hardens” or becomes immobile at early times. Using the linear solution, we find $u^{(s)}/\bar{u} \rightarrow -3/2R$ in the limit $Rt \rightarrow \infty$, for t finite. Here \bar{u} is the depth-averaged flow speed. Thus in this limit, we have a no-slip surface and consequently the decay time is four times the Orchard time scale, as in equation (9); this is in agreement with the slope of the $R=100$ results in Fig. 1. Note that $u^{(s)}$ is negative, indicating return flow to the crest. Flow reversal is predicted to occur at a critical time $t_c \approx (1/R)\ln(4R)$. For $R=1$, t_c is predicted to be 1.39. For comparison, FEM results show progressive flow reversal for times t over the range 1.1 to 1.7. The ultimate slope of the $R=1$ results in Fig. 1 corresponds closely to the value $\omega_1 = -0.134$, the root of smaller magnitude predicted by equation (7c).

Use of a set of physical units illustrates applicability to actual coatings. We choose the values $h_0=0.01$ cm, $\mu=10$ poise, $\sigma_0=30$ dynes/cm, and $D=10^{-5}$ cm²/sec.⁸ In Fig. 3 we show the amplitude ratio for an initial sinusoidal ripple plotted versus wavelength in cm at time=5 minutes, for $\Gamma/\sigma_0=0, 0.01$, and 0.1 using the linear theory. Leveling behavior is seen to generally follow the inverse k^4 law from (2) and the perfectly clean surface levels most quickly, as expected. If we suppose, however, that $\Gamma/\sigma_0=0.01$ represents an ‘irreducible’ amount of environmental contamination, it is seen that increasing the quantity of surface active ingredient can improve leveling for wavelengths less than about 0.5 cm.

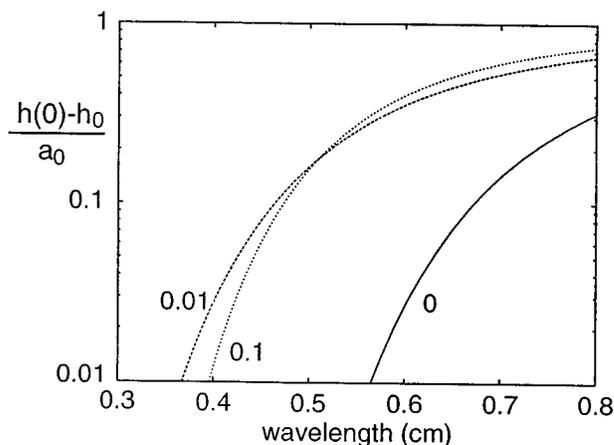


FIG. 3. Ripple amplitude ratio versus wavelength in cm at $t=5$ min for a clean surface and two levels of surfactant, using the linear theory with Γ/σ_0 values shown. The surface diffusion coefficient is 10^{-5} cm²/sec. See text for other parameter values.

While an increase in surfactant will only improve leveling over a restricted range of ripple wavelengths, such tailoring could be effective in practice, especially since particular application methods for coatings often produce only a narrow spectrum of disturbances. For example, for coatings produced by spreaders and rollers, the so-called ‘ribbing’ instability is known to lead to well-defined periodic trains of ripples.⁹

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^{a1}Author to whom correspondence should be addressed.

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